ANODE OXIDATION OF SOME HETEROCYCLIC ACIDS IN DIMETHYLFORMAMIDE

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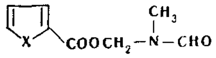
It is shown that the electrolysis of furan-2-carboxylic, thiophene-2-carboxylic, and selenophene-2-carboxylic acids in dimethylformamide on platinum electrodes gives N-(2-furoyloxymethyl)-N-methylformamide, N-(2-thenoyloxymethyl)-N-methylformamide, and N-(2-selenoyloxymethyl)-N-methylformamide, respectively.

In [1] it is pointed out that phenyl, benzoyl, and benzoate derivatives are obtained by the electrolysis of benzoic acid in dimethyl formamide in the presence of benzene or toluene and also in the presence of cyclohexene and furan. Proceeding from this, we decided to investigate the electrolysis of furan-2-carboxylic, thiophene-2-carboxylic, and selenophene-2-carboxylic acids in the presence of thiophene and furan, under similar conditions, in order to obtain the comparatively hard-to-obtain compounds of the 2-(2-selenoyl)thiophene, 2-(2-selenoyl)furan, and 2-(2-thenoyl)furan types. However, it had to be borne in mind that cleavage of the thiophene ring often occurs during the electrolysis of compounds of the thiophene series [2-4]. It seemed to us that the possible closing of the thiophene ring could be prevented if the electrolysis were carried out on platinum electrodes in dimethylformamide using lithium nitrate as the supporting electrolyte.

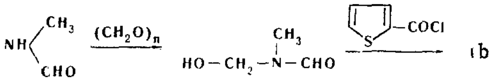
Under these conditions, the electrolysis of furan-2-carboxylic acid in a mixture containing an equimolecular amount of thiophene (or without it) led to N-(2-furoyloxymethyl)-N-methylformamide (Ia), while the electrolysis of thiophene-2-carboxylic acid, both in the presence and absence of furan, led to N-(2-thenoyloxymethyl)-N-methylformamide (Ib). The analogous compound Ic was also obtained from selenophene-2-carboxylic acid.



Ia-c

a X = O; b X = S; c X = Se

The structures of the products obtained were confirmed by their IR spectra (see Experimental), molecular-weight determinations, the results of elementary analysis, and (for Ib) also by alternative synthesis from N-hydroxymethyl-N-methylformamide:



The starting furan-2-carboxylic acid was obtained by refluxing Ia with aqeuous sodium hydroxide.

The mechanism of the formation of Ia-c is still not quite clear to us. In the course of the electrosynthesis, carried out at constant current density, the electrode potential, measured by means of a PPTV-1 potentiometer, varied from 2.6 to 2.9 V, with respect to a saturated calomel electrode (SCE) in the case of thiophene-2-carboxylic acid. The polarization curves demonstrated that CO oxidation of the background solution, and the acid occurs in this range of potentials. From these results, it can be assumed that the following anode processes occur:

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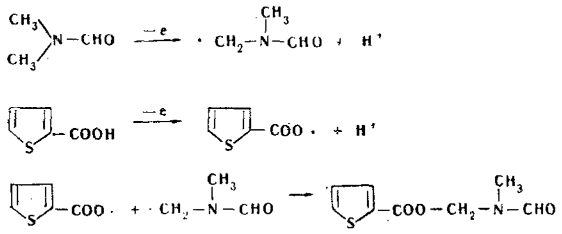

In addition to dimethylformamide, we also used dimethyl sulfoxide, but the starting carboxylic acids were recovered unchanged in all cases.

EXPERIMENTAL

The dimethylformamide and dimethyl sulfoxide were dried and distilled to give materials with n_D^{20} 1.4290 and 1.4756, respectively. The acids were synthesized by known methods and purified with respect to the literature melting points. The IR spectra of mineral oil suspensions of the samples were recorded with a UR-20 spectrometer with sodium chloride and lithium chloride prisms. The molecular weights were determined in benzene solution by the cryoscopic method. The electrosynthesis was carried out in a sealed 150-ml electrolytic cell equipped with two smooth platinum electrodes (3 × 3 cm) situated at a distance of 0.5 cm, a jacket for water cooling, a thermometer, a gas-removal tube, and a magnetic stirrer.

N-(Furoyloxymethyl)-N-methylformamide (Ia). A cell was charged with 120 ml of dimethylformamide, 9 g (0.08 mole) of furan-2-carboxylic acid, 6.7 g (0.08 mole) of thiophene, and 0.084 g of lithium nitrate, and a direct 250 mA current was passed through the cell at 20° for 19 h. The cell contents were filtered, and the filtrate was distilled at atmospheric pressure. The fraction with bp 80-130° was unchanged thiophene mixed with dimethylformamide. The dark, viscous residue obtained after removal of thiophene and dimethylformamide was extracted with benzene, and the benzene extract was washed successively with saturated sodium bicarbonate solution and water and dried over magnesium sulfate. The benzene was removed by distillation, and the residue was vacuum distilled. The fraction with bp 111-122° (0.085 mm), on standing in a refrigerator, was converted to a solid, slightly yellow product that was recrystallized from heptane–ether to give 3.2 g (22%) of Ia. Found %: C 52.4; H 5.0; mol. wt. 179. $C_8H_9NO_4$. Calculated %: C 52.5; H 5.0; mol. wt. 183.4. IR spectrum: 3160, 1720, 1690 cm^{-1} (CH of the furan ring, CO, and CHO).

Similar results were obtained in the electrolysis of furan-2-carboxylic acid in dimethylformamide in the absence of thiophene.

Hydrolysis of N-(Furoyloxymethyl)-N-methylformamide. A mixture of 1.8 g (0.01 mole) of Ia and 15 ml of 5% aqueous sodium hydroxide was refluxed for 1 h. The flask contents were cooled in ice water and acidified with 10% sulfuric acid. The resulting crystals were filtered, washed with water, and dried in a desiccator over magnesium sulfate. The product did not depress the melting point of an authentic sample of furan-2-carboxylic acid (mp 133°).

N-(2-Thenoyloxymethyl)-N-methylformamide (Ib). A. A cell was charged with 8.8 g (0.05 mole) of thiophene-2-carboxylic acid, 4.76 g (0.07 mole) of furan, 0.074 g of lithium nitrate, and 120 ml of dimethylformamide. A 250 mA current was passed through the cell for 17 h. The reaction mixture was worked up as in the case of Ia to give 2.8 g (21%) of Ib with bp 138-140° (0.8 mm) and mp 51-52°. The same results were obtained in the absence of furan. Found %: C 48.3; H 4.9; S 16.2; mol. wt. 192. $C_8H_9NO_3S$. Calculated %: C 48.2; H 4.6; S 16.1; mol. wt. 199.2. IR spectrum: 3090, 1690, 1670 cm^{-1} (CH of the thiophene ring, CO, and CHO).

B. A mixture of 29.8 g of N-methylformamide, 15.5 g of paraformaldehyde, 0.5 g of potassium carbonate, and 50 ml of absolute alcohol was refluxed for 1 h on a glycerol bath (bath temperature 110°). The alcohol was removed by distillation, and the residue was washed with absolute ether. The ether-insoluble, colorless oil was N-hydroxymethyl-N-methylformamide [5] which, without prior purification,* was used to obtain Ib.

A mixture of 17.7 g (0.24 mole) of N-hydroxymethyl-N-methylformamide, 13.8 g (0.1 mole) of thiophene-2-carboxylic acid chloride, and 100 ml of 5% sodium hydroxide was stirred for 30 min in ice water.

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*The compound was thermally unstable and, therefore, could not be vacuum distilled.

The reaction product was extracted three times with benzene, and the benzene extract was washed successively with saturated sodium bicarbonate and water and dried over magnesium sulfate. The benzene was removed by distillation, and the residue was vacuum distilled at 0.1 mm. The fraction with bp 137-142° [5.9 g (32%)] solidified at room temperature upon seeding with N-(2-thenoyloxymethyl)-N-methylformamide. Recrystallization from diethyl ether–heptane gave a substance with mp 51-52° that did not depress the melting point of Ib obtained by method A.

N-(2-Selenoyloxymethyl)-N-methylformamide (Ic). A cell was charged with 8.75 g (0.05 mole) of selenophene-2-carboxylic acid, 0.072 g of lithium nitrate, and 120 ml of dimethylformamide. A 250 mA current was passed through the mixture for 22 h. The mixture gradually darkened, and selenium was deposited on the anode. After similar workup, the product was purified by double vacuum distillation to give 4.2 g (36%) of Ic with bp 161-165° (0.8 mm), bp 136-137° (0.08 mm), and n_D^{20} 1.5778. Found %: C 39.0; H 3.8; mol. wt. 241. $C_8H_9NO_3Se$. Calculated %: C 39.0; H 3.7; mol. wt. 246.1.

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